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Theoretical Characterization of the Surface Composition of Ruthenium Nanoparticles in Equilibrium with Syngas

Supplementary Informations

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S1 Faceting of large RuNPs

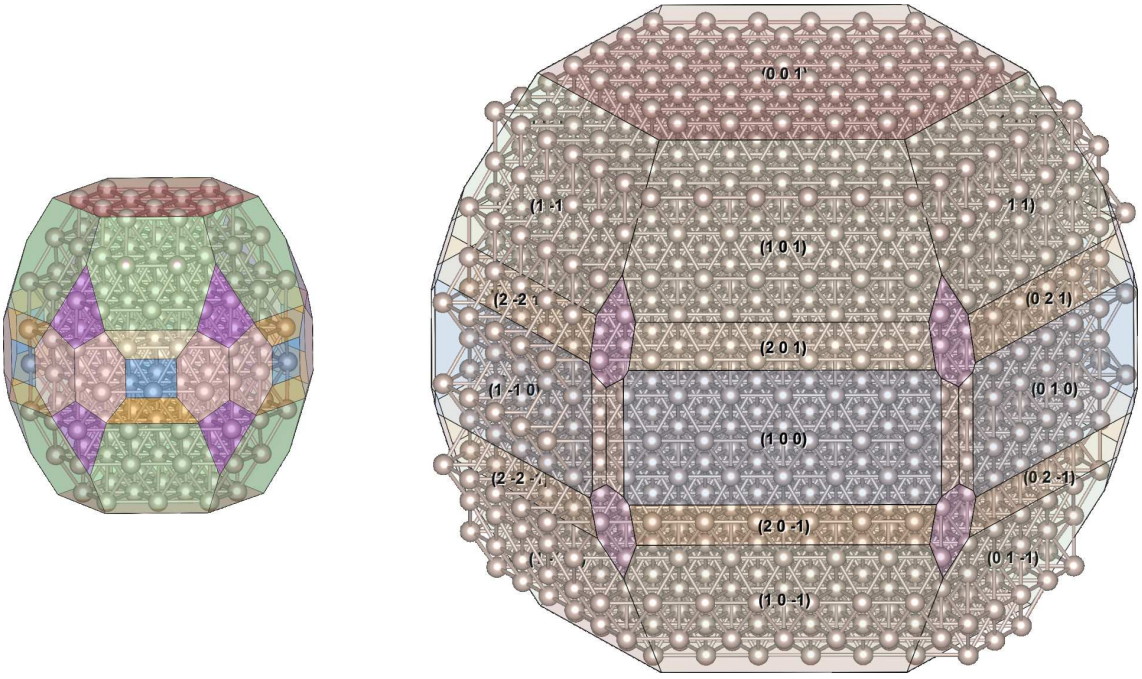


Figure S1: Left panel: Wulff construction of a bare 1.6 nm hcp RuNP. Right panel: Wulff construction of a bare 3 nm hcp RuNP, with B5 sites between the (001) and (101) crystallographic planes (adapted from Honkala *et al* (2005), *Science*, **307**, 555-558).

S2 Single H and CO adsorption on a RuNP. Low coverage

S2.1 Optimized geometries and adsorption energies

Table S1: **Ruthenium-Hydrogen distances for the Ru_{55} isomers**

Coordination type	Isomer	d_{H-Ru} (Å)
η	5^H	1.66
η	6^H	1.65
η	8^H	1.65
μ	7^H	1.87 / 1.78
μ	4^H	1.83 / 1.81
μ	1^H	1.83 / 1.81
μ	11^H	1.93 / 1.73
μ_3	2^H	1.97 / 1.92 / 1.90
μ_3	10^H	1.95 / 1.93 / 1.91
μ_3	3^H	1.98 / 1.95 / 1.81
μ_3	9^H	2.01 / 1.92 /1.92

Table S2: **H_2 dissociative adsorption energies (kcal.mol^{-1}) at several surface sites of Ru_{55}.**

Coordination type	Isomer	E_{ads} on Ru_{55}
η	5^H	-9.8
η	6^H	-6.5
η	8^H	-5.8
μ	7^H	-14.9
μ	4^H	-13.8
μ	1^H	-12.8
μ	11^H	-5.6
μ_3	2^H	-13.8
μ_3	10^H	-13.5
μ_3	3^H	-11.5
μ_3	9^H	-11.6

Table S3: **CO molecular adsorption energies (kcal.mol^{-1}) at several surface sites of Ru_{55}.**

Coordination type	Isomer	E_{ads} on Ru_{55}
η	2^{CO}	-49.8
η	11^{CO}	-49.4
η	1^{CO}	-46.5
η	7^{CO}	-45.4
η	5^{CO}	-42.6
η	9^{CO}	-46.6
η	2^{OC}	-3.9
μ	10^{CO}	-52.7
μ	8^{CO}	-45.4
μ_4	6^{CO}	-43.9
(η,η^2)	3^{CO}	-46.9
(η,η^2)	4^{CO}	-40.3

Table S4: **Ruthenium-Carbon distances for the Ru_{55} isomers. Values with * correspond to Ruthenium-Oxygen distances.**

Coordination type	Isomer	d_{CO-Ru} (Å)
η	2^{CO}	1.87
η	11^{CO}	1.87
η	1^{CO}	1.86
η	7^{CO}	1.89
η	5^{CO}	1.89
η	9^{CO}	1.86
η	2^{OC}	2.19*
μ	10^{CO}	2.05 / 2.04
μ	8^{CO}	2.07 / 2.04
μ_4	6^{CO}	2.33 / 2.33 / 2.20 / 2.11
(η, η^2)	3^{CO}	2.38 / 2.09 / 1.98 / 2.26*
(η, η^2)	4^{CO}	2.49 / 2.31 / 2.05 / 1.97 / 2.20*

S2.2 Multicarbonyl sites at apex location

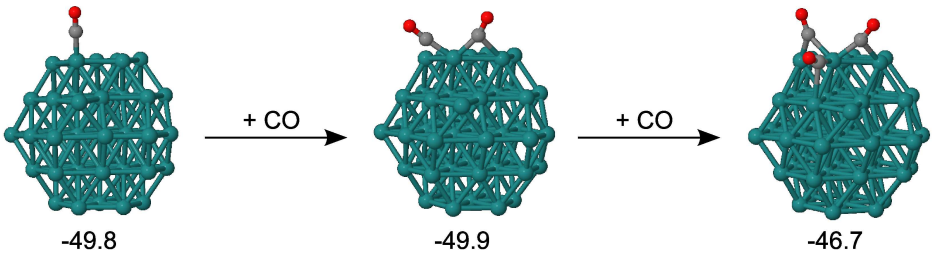


Figure S2: Geometries and adsorption energies per CO in kcal.mol^{-1} for $\mathbf{2}^{\mathrm{CO}}$, $\mathbf{2}^{\mathrm{2CO}}$ and $\mathbf{2}^{\mathrm{3CO}}$.

S2.3 DOS and COHP profiles for CO*Ru$_{55}$

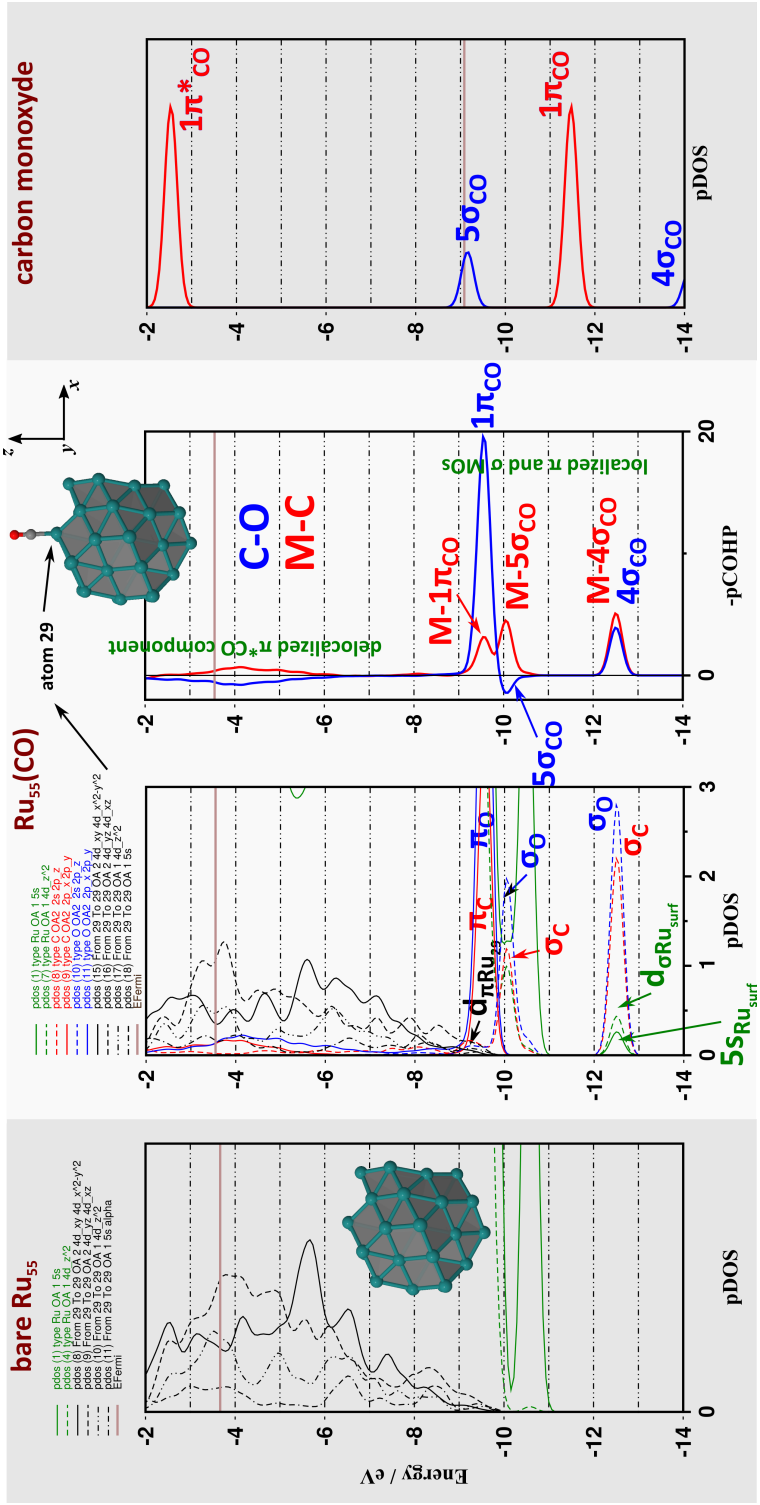
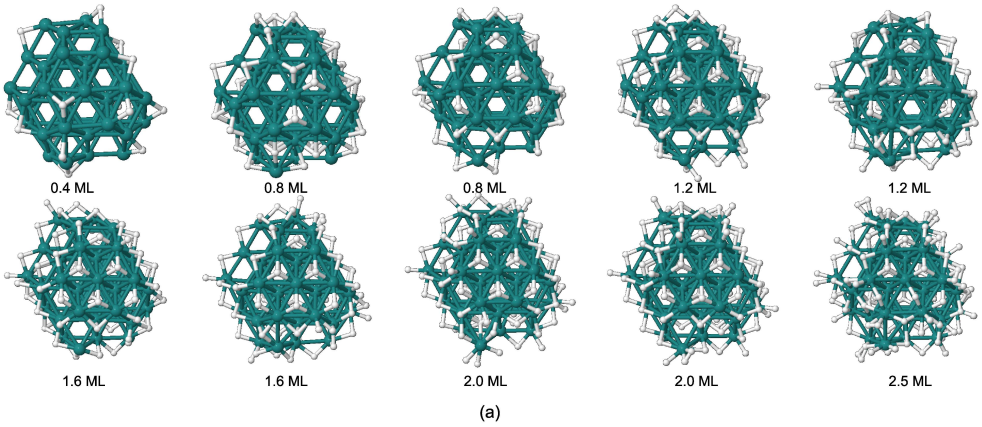


Figure S3: pCOHP and pDOS for $\mathbf{2}_{\mathrm{Ru}}^{\mathrm{CO}}$, compared to the pDOS of CO and of the Ru$_{55}$ moiety, frozen in the geometry of $\mathbf{2}_{\mathrm{Ru}}^{\mathrm{CO}}$.

S3 Single H and CO adsorption on a RuNP. High coverages

S3.1 Optimized geometries



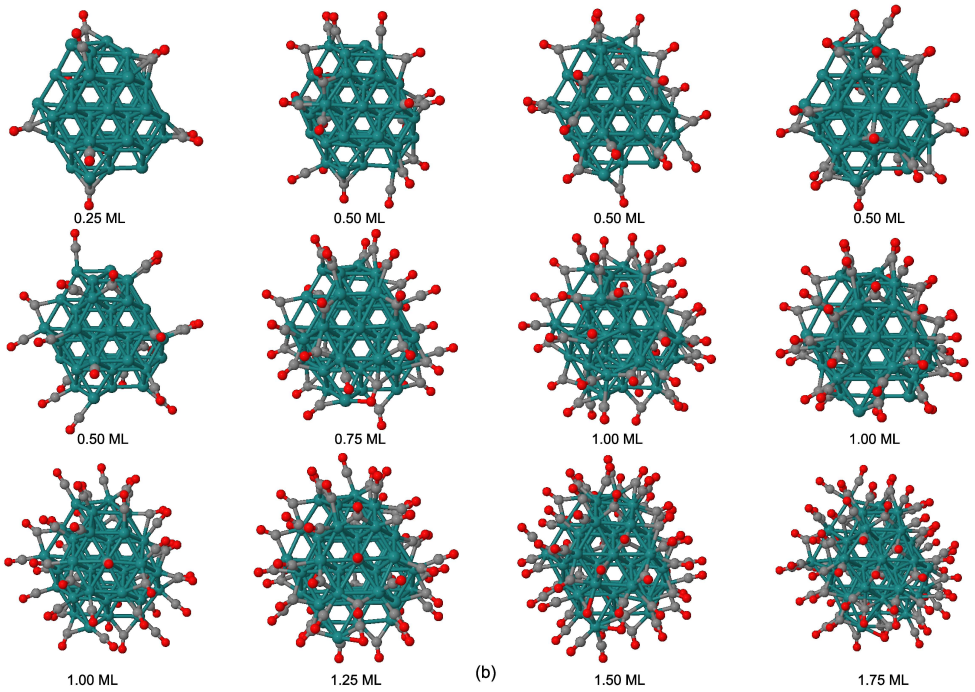


Figure S4: DFT-optimized high coverages RuNP H (a) CO (b). Owing to the reduced scale, hydrogenated RuNPs with subsurface H are not shown here, since they are much alike the RuNPs plotted here.

S3.2 Energies and coordination modes

coverage	H coord.	E_{DFT}	E_{ads}
0.4 ML	11 μ 6 μ_3	-492.69	-14.83
0.4 ML + subsurface	16 μ 7 μ_3 3 Oh	-525.13	-11.31
0.8 ML_1	22 μ 13 μ_3	-564.40	-14.41
0.8 ML_1+ subsurface	19 μ 18 μ_3 7 Oh	-591.93	-9.76
0.8 ML $_2$	24 μ 12 μ_3	-567.59	-13.89
0.8 ML_2+ subsurface	22 μ 16 μ_3 7 Oh	-595.17	-9.46
1.2 ML_1	2 η 34 μ 17 μ_3	-634.13	-13.42
1.2 ML_1+ subsurface	2 η 30 μ 21 μ_3 9 Oh	-659.14	-9.26
1.2 ML_2	2 η 37 μ 14 μ_3	-634.19	-13.44
1.2 ML_2+ subsurface	2 η 32 μ 18 μ_3 1 μ_4 9 Oh	-659.40	-9.35
1.6 ML_1	6 η 43 μ 21 μ_3	-696.53	-11.80
1.6 ML_1+ subsurface	5 η 44 μ 21 μ_3 9 Oh	-722.91	-9.08
1.6 ML_2	8 η 45 μ 17 μ_3	-697.69	-12.19
1.6 ML_2+ subsurface	8 η 42 μ 20 μ_3 9 Oh	-723.81	-9.35
2.0 ML_1	16 η 57 μ 14 μ_3 1 μ_4	-760.59	-10.26
2.0 ML_1+subsurface	17 η 53 μ 17 μ_3 9 Oh	-784.30	-8.40
2.0 ML_2	16 η 52 μ 20 μ_3	-761.26	-10.43
2.0 ML_2+ subsurface	17 η 52 μ 19 μ_3 9 Oh	-788.69	-8.55
2.5 ML	22 η 49 μ 15 μ_3 12 H_2	-839.13	-9.10

Table S5: **H coordination modes for each considered coverage. E_{DFT} is given in eV and E_{ads} in kcal.mol^{-1}.**

coverage	CO coord.	E_{DFT}	E_{ads}
0.25 ML	1 η 6 μ 4 μ_3	-610.75	-49.99
0.50 ML_1	5 η 15 μ 2 μ_3	-795.40	-48.18
0.50 ML_2	9 η 10 μ 3 μ_3	-794.98	-47.74
0.50 ML_3	1 η 14 μ 7 μ_3	-796.15	-48.97
0.50 ML_4	18 η 4 μ	-794.70	-47.44
0.75 ML	7 η 18 μ 7 μ_3 1 (η, η^2)	-979.52	-47.21
1.00 ML_1	9 η 30 μ 4 (η, η^2)	-1144.42	-45.42
1.00 ML_2	18 η 21 μ 4 μ_3	-1143.74	-45.06
1.00 ML_3	26 η 15 μ 2 μ_3	-1143.14	-44.74
1.25 ML	17 η 32 μ 5 μ_3 1 (η, η^2)	-1339.14	-42.81
1.50 ML	25 η 34 μ 5 μ_3 1 (η, η^2)	-1514.09	-40.02
1.75 ML	35 η 33 μ 5 μ_3 2 (η, η^2)	-1651.27	-36.51

Table S6: **CO coordination modes for each considered coverage. E_{DFT} is given in eV and E_{ads} in kcal.mol^{-1}.**

S4 Phase diagrams without ZPE corrections

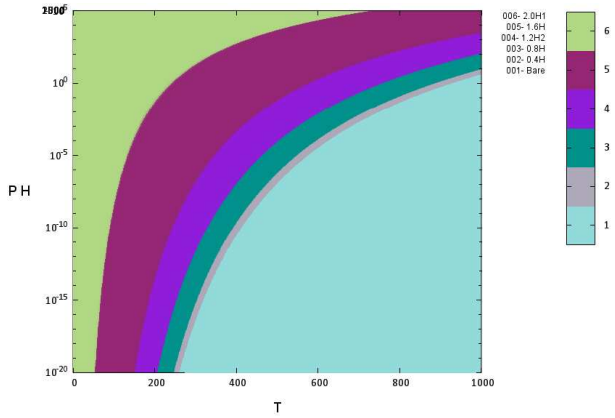


Figure S5: $(T, p_{\mathrm{H_2}})$ phase diagram for H_2 adsorption on the 55-atoms RuNP without ZPE corrections

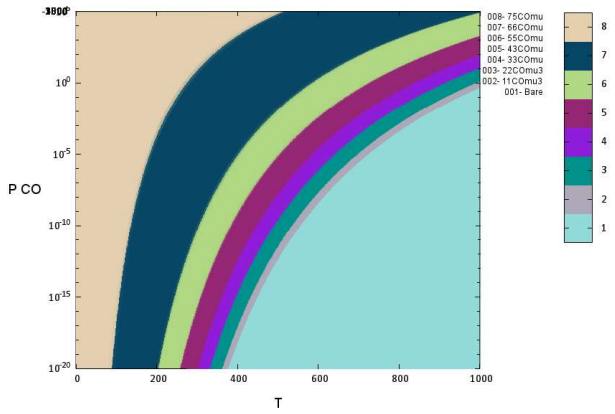


Figure S6: (T, p_{CO}) phase diagram for CO adsorption on the 55-atoms RuNP without ZPE corrections.

S5 H and CO co-adsorption on a RuNP

S5.1 Optimized geometries

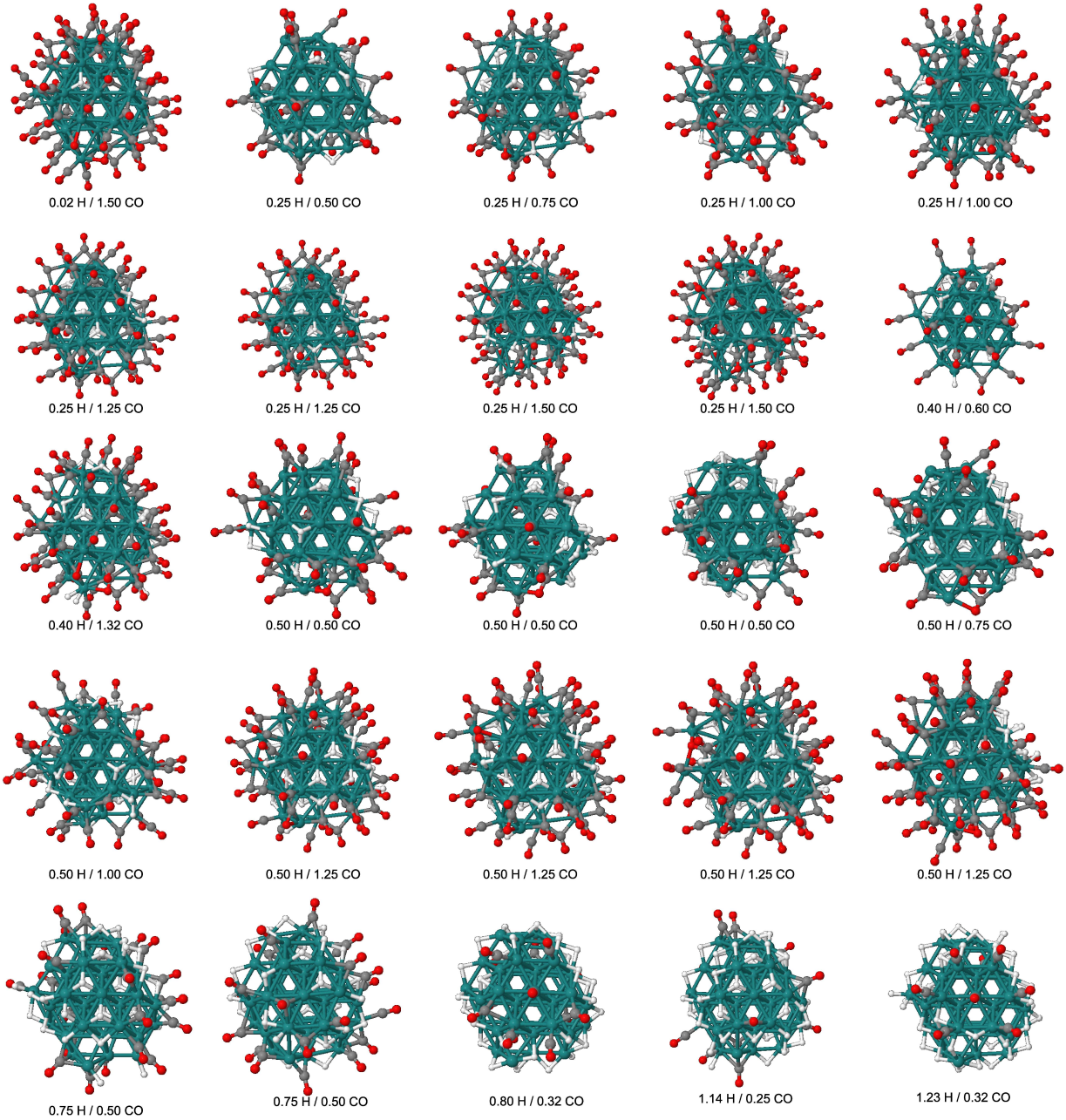


Figure S7: DFT-optimized high coverages RuNP H and CO.

S5.2 Adsorption energies and coordination modes

Table S7: **H/CO coordination modes for each considered coverage. E_{DFT} is given in eV and E_{ads} in kcal.mol^{-1}.**

coverage	H coord.	CO coord.	E_{DFT}	E_{ads}
0.02/1.50 ML	1 μ_3	25 η 34 η 6 μ_3 1 (η,η^2)	-1517.55	-39.4
0.25/0.50 ML	7 μ 4 μ_3	1 η 16 μ 5 μ_3	-839.64	-37.09
0.25/0.75 ML$_1$	4 μ 7 μ_3	6 η 19 μ 7 μ_3 1 (η,η^2)	-1021.63	-38.02
0.25/0.75 ML$_2$	5 μ 6 μ_3	29 η 4 μ	-1018.90	-36.58
0.25/1.00 ML$_1$	5 μ 5 μ_3 1 μ^4	22 η 18 μ 3 μ_3	-1185.21	-37.73
0.25/1.00 ML$_2$	1 η 7 μ 3 μ_3	14 η 28 μ 1 μ_3	-1185.42	-37.82
0.25/1.25 ML	1 η 4 μ 5 μ_3 1 μ_4	13 η 35 μ 6 μ_3 1 (η,η^2)	-1378.06	-36.30
0.25/1.50 ML$_1$	1 η 7 μ 3 μ_3	27 η 34 μ 6 μ_3 1 (η,η^2)	-1550.22	-33.99
0.25/1.50 ML$_2$	1 η 3 μ 6 μ_3 1 Oh	28 η 33 μ 4 μ_3 1 (η,η^2)	-1550.06	-33.93
0.40/0.60 ML	1 η 14 μ 2 μ_3 1 μ_4	20 η 4 μ 1 μ_3	-914.48	-32.15
0.40/1.30 ML	1 η 1 μ 8 H_2	18 η 32 μ 6 μ_3 2 μ_4	-1447.99	-31.91
0.50/0.50 ML$_1$	12 μ 10 μ_3	5 η 11 μ 5 μ_3 1 (η,η^2)	-880.82	-29.93
0.50/0.50 ML$_2$	16 μ 6 μ_3	3 η 10 μ 7 μ_3 1 (η,η^2) 1 μ_4	-881.16	-30.11
0.50/0.50 ML$_3$	8 μ 14 μ_3	20 η 2 μ	-879.11	-29.03
0.50/0.50 ML$_4$	1 η 12 μ 9 μ_3	8 η 11 μ 3 μ_3	-880.33	-29.68
0.50/0.75 ML	13 μ 9 μ_3	16 η 14 μ 2 μ_3 1 (η,η^2)	-1062.19	-31.85
0.50/1.00 ML	2 η 9 μ 9 μ_3 2 μ^4	26 η 11 μ 6 μ_3	-1223.69	-31.82
0.50/1.25 ML$_1$	1 η 6 μ 13 μ_3 2 μ^4	22 η 29 μ 3 μ_3 1 (η,η^2)	-1415.94	-31.33
0.50/1.25 ML$_2$	5 η 6 μ 11 μ_3	20 η 31 μ 4 μ_3	-1415.84	-31.31
0.75/0.50 ML$_1$	4 η 17 μ 12 μ_3	4 η 14 μ 4 μ_3	-921.99	-25.64
0.75/0.50 ML$_2$	1 η 22 μ 9 μ_3 1 μ_4	4 η 12 μ 6 μ_3	-922.91	-26.03
0.82/0.32 ML	20 μ 16 μ_3	10 η 4 μ	-801.33	-22.40
1.14/0.25 ML	2 η 31 μ 17 μ_3	1 η 4 μ 6 μ_3	-804.73	-18.54
1.23/0.32 ML	1 η 31 μ 18 μ_3 2 μ_4	14 η	-868.21	-18.54

S5.3 Surface-subsurface H diffusion

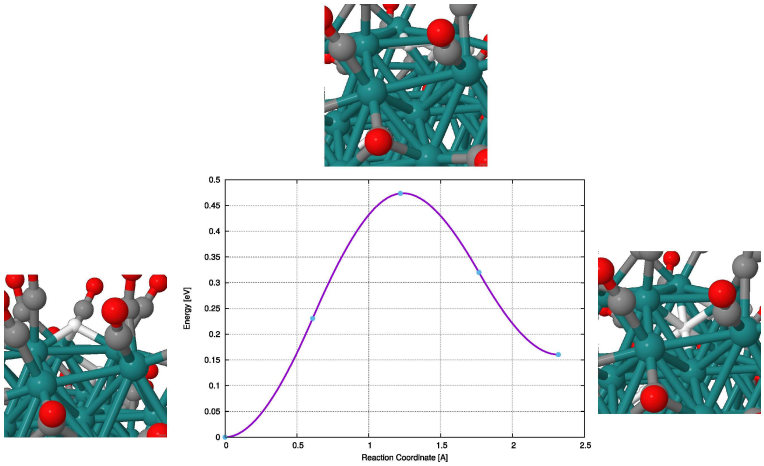


Figure S8: Fcc site - octahedral site diffusion in $Ru_{55}H_{11}(CO)_{66}$.

S6 Phase diagrams: empirical variation of the adsorption energies

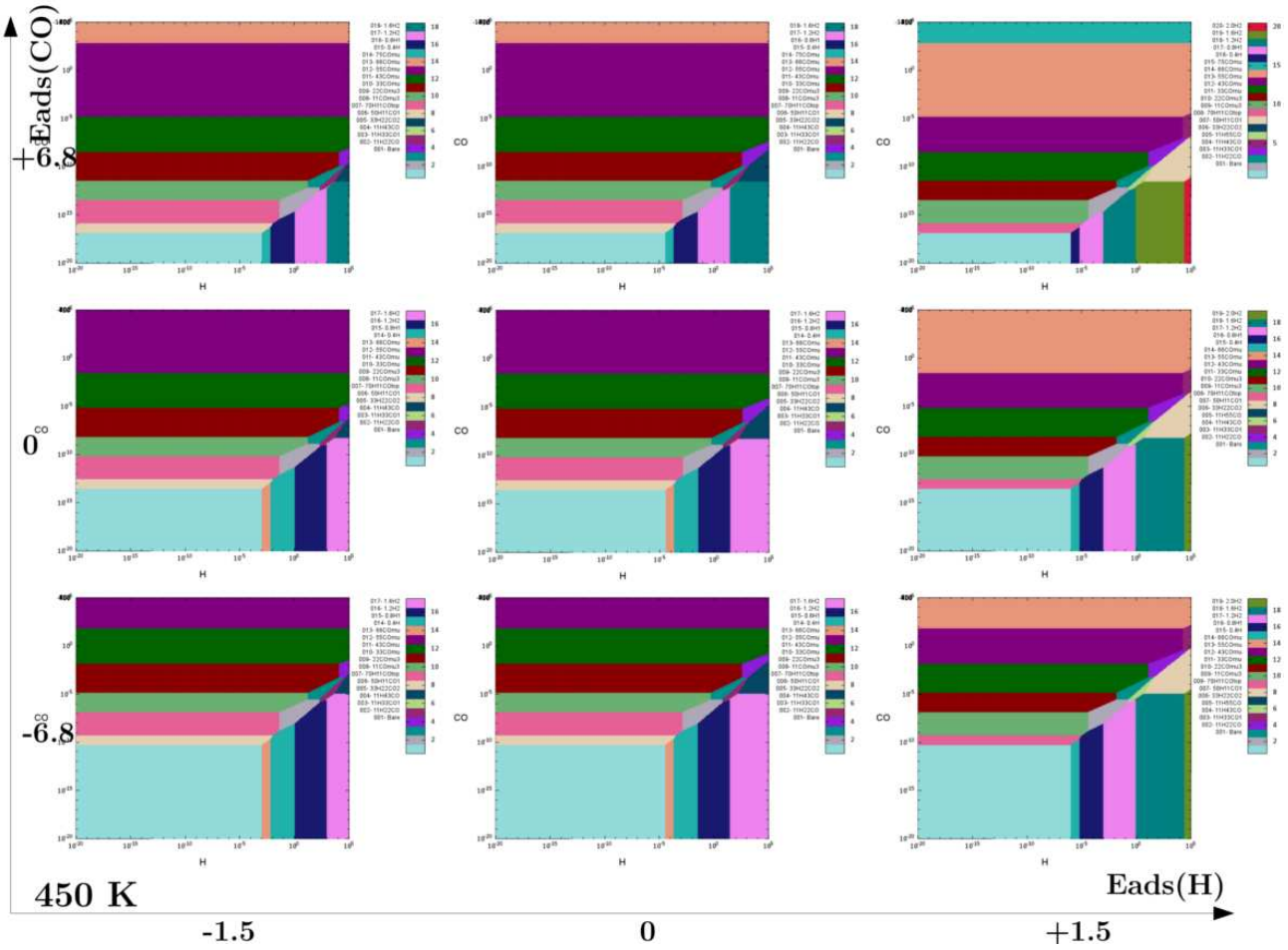


Figure S9: Phase diagram for H_2 and CO adsorption on RuNP at 450 K with variation of adsorption energies : $E_{ads}(H_2)\pm1.5$ kcal.mol^{-1} and $E_{ads}(CO) \pm 6.8$ kcal.mol^{-1}

S7 Discussion

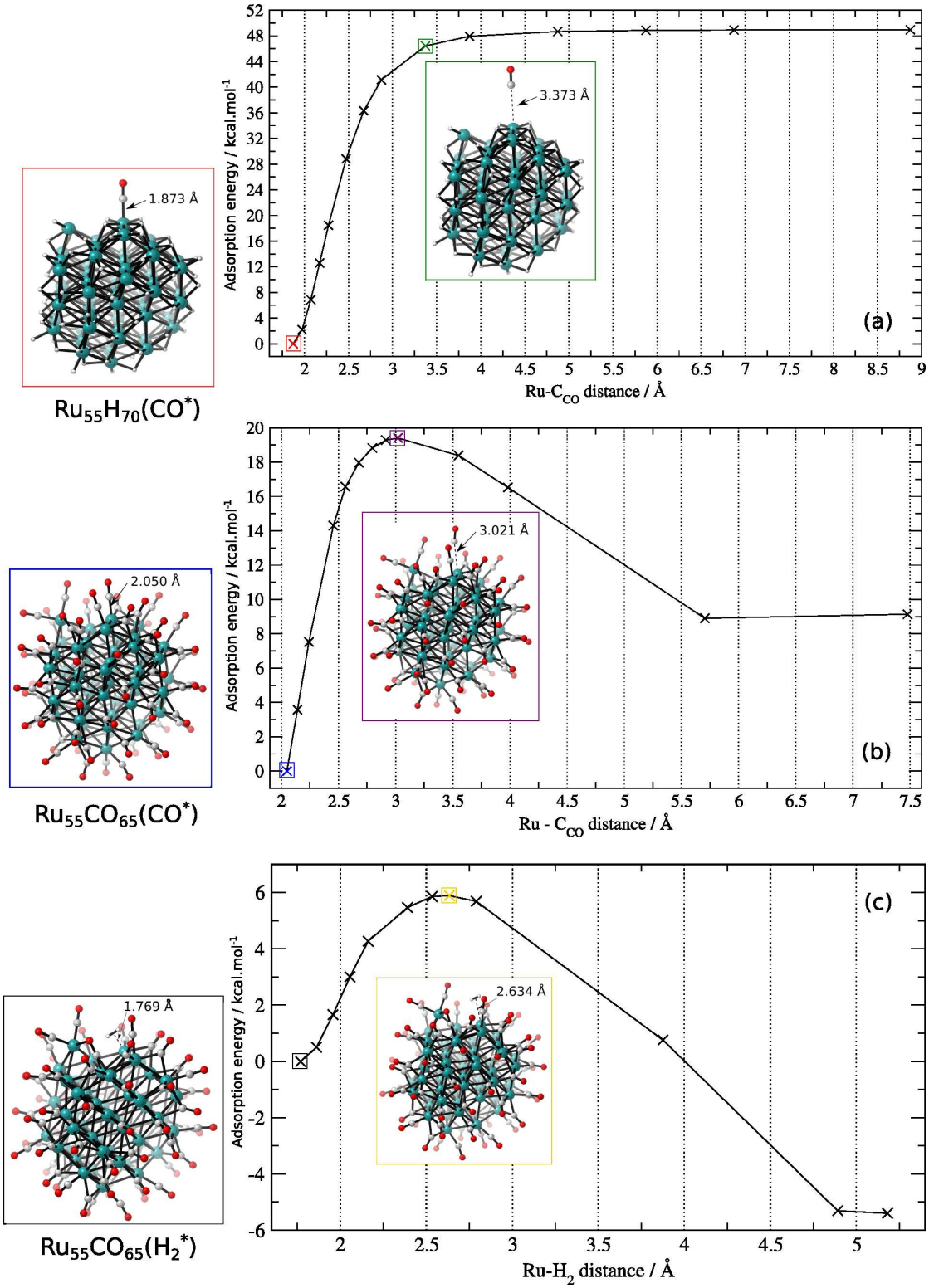


Figure S10: Surface energy scans. (a) adsorption of CO on $Ru_{55}(H)_{70}$; (b) adsorption of CO on $Ru_{55}(CO)_{65}$; (c) adsorption of H_2 on $Ru_{55}(CO)_{65}$ (the Ru_{55} core was kept frozen).

Quantification of hydrides adsorbed on RuNPs@PVP pressurized with 3 bar of syngas (1:1 molar mixture of H_2 and CO) and heated at 80 and 150 °C

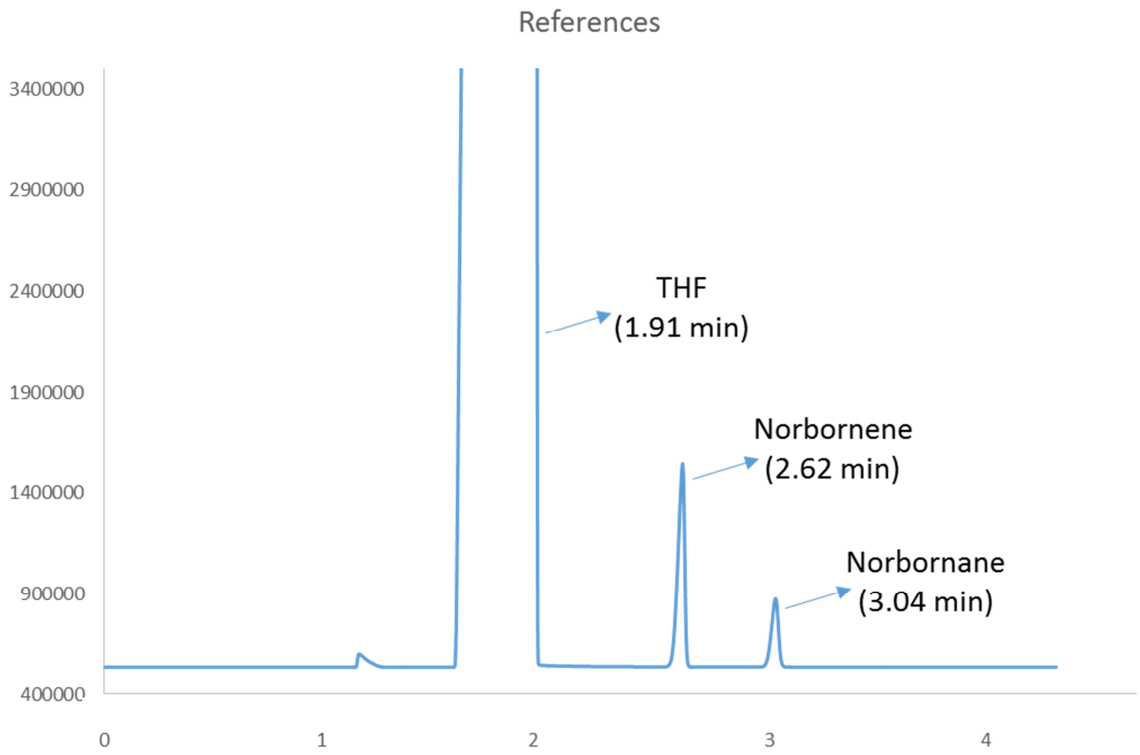


Figure S8: Gas chromatography spectrum of a reference mixture solution (THF, 2-norbornene and norbornane).

LMP57 (150 °C)

Following the experimental procedure published in *ACS Catalysis* **2014**, *4*, 3016, a 2 mL quick pressure valve NMR tubes was filled with 20 mg of RuNPs@PVP (~ 8% Ru), pressurized with 3 bar of syngas (1:1 molar mixture of H_2 and CO) and heated at 150 °C for 24 h.

After this, we quantified the hydrides adsorbed following a previously reported procedure (*Angew. Chem. Int. Ed.* **2008**, *47*, 2074-2078). The NMR tube was depressurized at 150 °C. The Ru/PVP (20 mg) were re-dispersed in 2 mL of THF and reacted with 2-norbornene (7.5 mg, 0.08 mmol, 5 equiv.). The amount of norbornane formed was measured by G.C. analysis.

After 24h of vigorous stirring in a 10 ml flask, only traces of norbornane was observed by G.C, confirming that there are not hydrides adsorbed at ruthenium surface after these conditions.

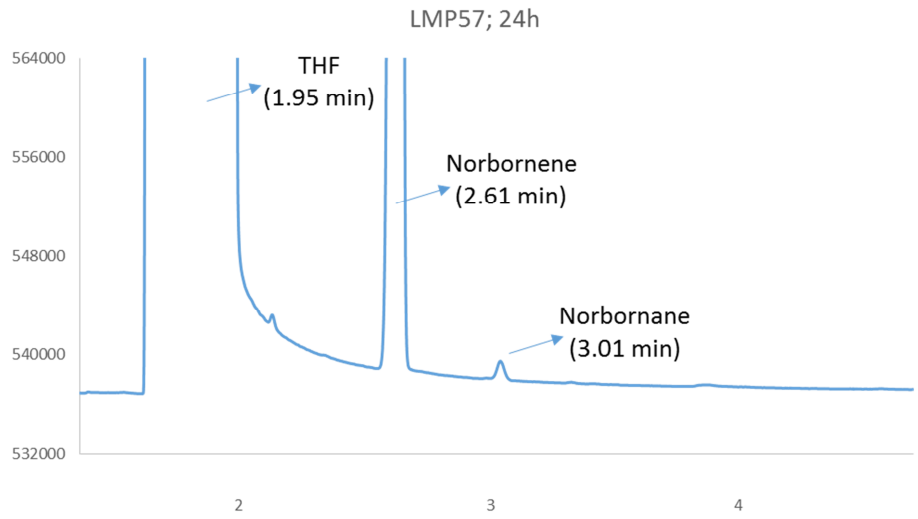


Figure S9: Gas chromatography spectrum recorded after reaction of 7.5 mg of 2-norbornene with 20 mg of RuNPs@PVP in a 2 mL quick pressure valve NMR tube obtained after 3 bar of syngas at 150 °C (1:1 molar mixture of H_2 and CO).

Compound	r.t.	area	%
THF	1.95	3295536	-
2-norbornene	2.61	18111	99.86
norbornane	3.01	25	0.14

Calculation of hydrides adsorbed on RuNPs@PVP:

RuNPs@PVP (~8 % Ru):
Size = 1.3 (0.2) nm
Total Atoms = 114
Core atoms = 36
Surface atoms = 78
% Surface atoms = 68 %

1) 20 mg de RuNPs@PVP → 0.016 mmol Ru → 0.011 mmol Ru_s

2) Norbornane consumed = 0.08 mmol (initial norbornene) * 0.14 (% norbornane formed)*0.01 = 0.00011 mmol
3) Hydrides/surface atom = 0.00011/0.011 = 0.01

LMP58 (80 °C)

Following the experimental procedure published in *ACS Catalysis* **2014**, *4*, 3016, a 2 mL quick pressure valve NMR tubes was filled with 20 mg of RuNPs@PVP (~ 8% Ru), pressurized with 3 bar of syngas (1:1 molar mixture of H_2 and CO) and heated at 80 °C for 24 h.

After this, we quantified the hydrides adsorbed following a previously reported procedure (*Angew. Chem. Int. Ed.* **2008**, *47*, 2074-2078). The NMR tube was depressurized at 80 °C. The Ru/PVP (20 mg) were re-dispersed in 2 mL of THF and reacted with 2-norbornene (7.5 mg, 0.08 mmol, 5 equiv.). The amount of norbornane formed was measured by G.C. analysis.

After 24h of vigorous stirring in a 10 ml flask, only traces of norbornane was observed by G.C, confirming that there are not hydrides adsorbed at ruthenium surface after these conditions.

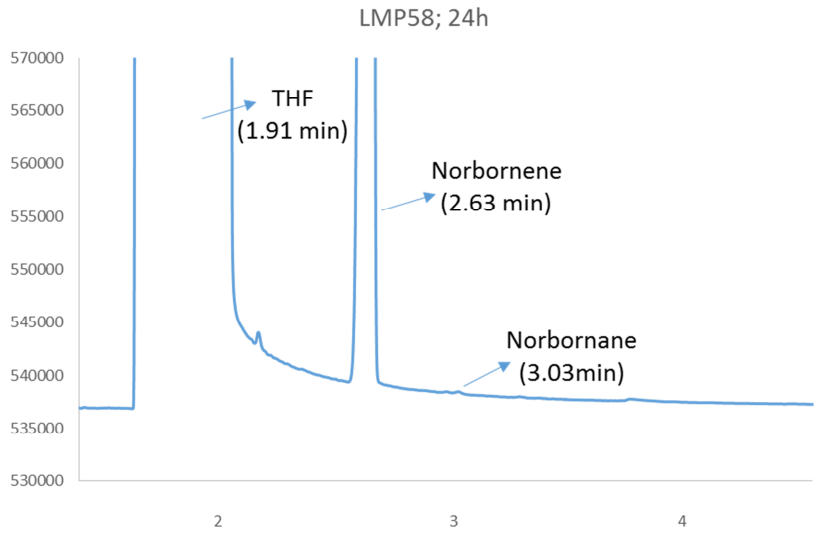


Figure S10: Gas chromatography spectrum recorded after reaction of 7.5 mg of 2-norbornene with 20 mg of RuNPs@PVP in a 2 mL quick pressure valve NMR tube obtained after 3 bar of syngas at 80 °C (1:1 molar mixture of H_2 and CO).

Compound	r.t.	area	%
THF	1.91	4522913	-
2-norbornene	2.63	29040	99.99
norbornane	3.03	2.7	0.01

Calculation of hydrides adsorbed on RuNPs@PVP:

RuNPs@PVP (~8 % Ru):
Size = 1.3 (0.2) nm
Total Atoms = 114
Core atoms = 36
Surface atoms = 78

% Surface atoms = 68 %

1) 20 mg de RuNPs@PVP → 0.016 mmol Ru → 0.011 mmol Ru_s
2) Norbornane consumed = 0.08 mmol (initial norbornene) * 0.01 (% norbornane formed)*0.01 = 0.000008 mmol
3) Hydrides/surface atom = 0.000008/0.011 = 0.0007

LMP60 (150 °C)

Following the experimental procedure published in *ACS Catalysis* **2014**, *4*, 3016, a Fischer-Porter (80 mL) was filled with 100 mg of RuNPs@PVP (~ 8% Ru), pressurized with 3 bar of syngas (1:1 molar mixture of H_2 and CO) and heated at 150 °C for 24 h.

After this, we quantified the hydrides adsorbed following a previously reported procedure (*Angew. Chem. Int. Ed.* **2008**, *47*, 2074-2078). The Fischer-Porter was depressurized at 150 °C. After that, the Ru/PVP (100 mg) were re-dispersed in 10 mL of THF and reacted with 2-norbornene (37.5 mg, 0.4 mmol, 5 equiv.). The amount of norbornane formed was measured by G.C. analysis.

After 24h of vigorous stirring in a 80 ml flask, only traces of norbornane was observed by G.C, confirming that there are not hydrides adsorbed at ruthenium surface after these conditions.

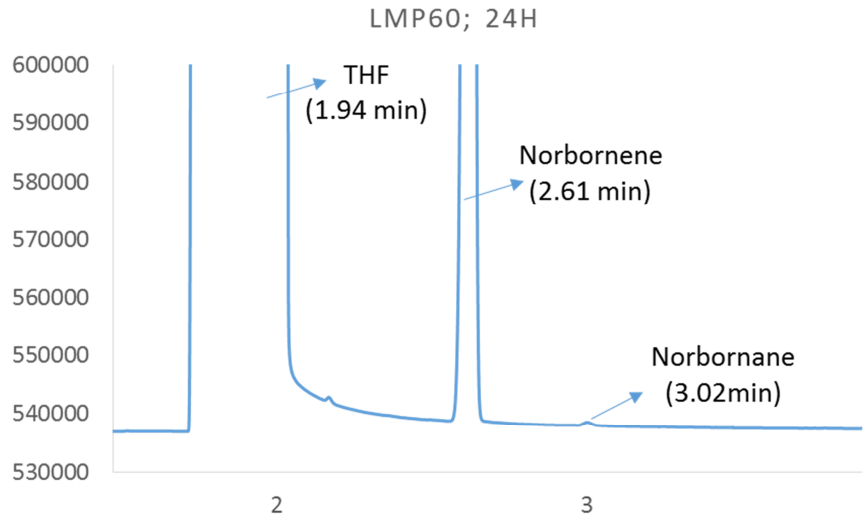


Figure S11: Gas chromatography spectrum recorded after reaction of 37.5 mg of 2-norbornene with 100 mg of RuNPs@PVP in a 80 mL Fischer-Porter obtained after 3 bar of syngas at 80 °C (1:1 molar mixture of H_2 and CO).

Compound	r.t.	area	%
THF	1.94	2930334	-
2-norbornene	2.61	15277	99.93
norbornane	3.02	11	0.07

Calculation of hydrides adsorbed on RuNPs@PVP:

RuNPs@PVP (~8 % Ru):
Size = 1.3 (0.2) nm
Total Atoms = 114

Core atoms = 36
Surface atoms = 78
% Surface atoms = 68 %

1) 100 mg de RuNPs@PVP → 0.08 mmol Ru → 0.054 mmol Ru_s
2) Norbornane consumed = 0.4 mmol (initial norbornene) * 0.07 (% norbornane formed)*0.01 = 0.0003 mmol
3) Hydrides/surface atom = 0.0003/0.054 = 0.005

LMP61 (80 °C)

Following the experimental procedure published in *ACS Catalysis* **2014**, *4*, 3016, a Fischer-Porter (80 mL) was filled with 100 mg of RuNPs@PVP (~ 8% Ru), pressurized with 3 bar of syngas (1:1 molar mixture of H_2 and CO) and heated at 80 °C for 24 h.

After this, we quantified the hydrides adsorbed following a previously reported procedure (*Angew. Chem. Int. Ed.* **2008**, *47*, 2074-2078). The Fischer-Porter was depressurized at 80 °C. After that, the Ru/PVP (100 mg) were re-dispersed in 10 mL of THF and reacted with 2-norbornene (37.5 mg, 0.4 mmol, 5 equiv.). The amount of norbornane formed was measured by G.C. analysis.

After 24h of vigorous stirring in a 80 ml flask, only traces of norbornane was observed by G.C, confirming that there are not hydrides adsorbed at ruthenium surface after these conditions.

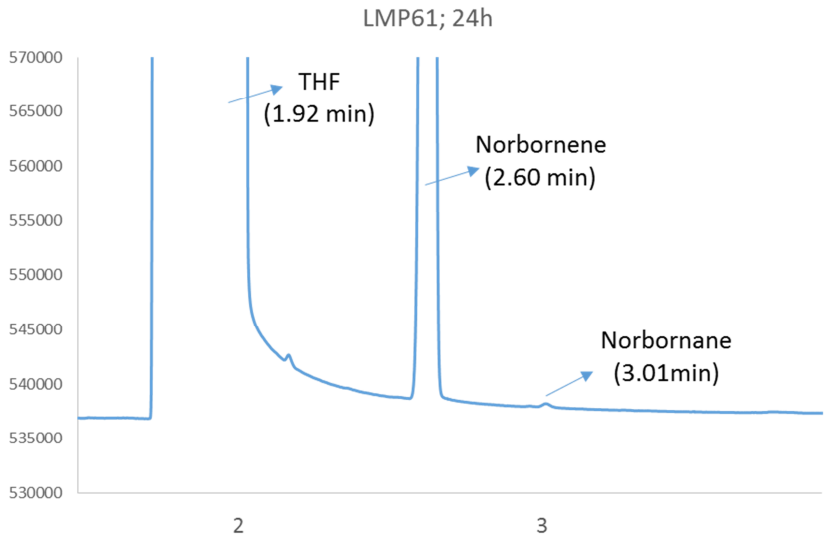


Figure S12: Gas chromatography spectrum recorded after reaction of 37.5 mg of 2-norbornene with 100 mg of RuNPs@PVP in a 80 mL Fischer-Porter obtained after 3 bar of syngas at 80 °C (1:1 molar mixture of H_2 and CO).

Compound	r.t.	area	%
THF	1.92	2840934	-
2-norbornene	2.60	17235	99.97
norbornane	3.01	6	0.03

Calculation of hydrides adsorbed on RuNPs@PVP:

RuNPs@PVP (~8 % Ru):

Size = 1.3 (0.2) nm
Total Atoms = 114
Core atoms = 36
Surface atoms = 78
% Surface atoms = 68 %

1) 100 mg de RuNPs@PVP → 0.08 mmol Ru → 0.054 mmol Ru_s
2) Norbornane consumed = 0.4 mmol (initial norbornene) * 0.034 (% norbornane formed)*0.01 = 0.00014 mmol
3) Hydrides/surface atom = 0.00014/0.054 = 0.0026